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Three dimensional (3D) printed electrodes for interdigitated supercapacitors

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Abstract

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Keywords

interdigitated, electrodes, supercapacitors, printed, three, 3d, dimensional

Disciplines

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Three Dimensional (3D) Printed Electrodes for Novel Interdigitated Supercapacitors

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Abstract

Common fabrication techniques typically require multiple and complex MEMS processing steps to create 3D electrode architectures. Here we report on the use of metal printing based on Selective Laser Melting (SLM) technology to produce 3D titanium interdigitated electrodes. This was used as a platform to deposit polypyrrole and the resultant structure was evaluated for use as a capacitive electrode. We also demonstrate a solid-state interdigitated supercapacitor using a poly(vinyl alcohol) (PVA)-H_3PO_4 polymer electrolyte.

Highlights:

- 3D interdigitated electrodes are fabricated through Selective Laser Melting Additive Fabrication.

- The 3D electrodes demonstrate a comparable performance to those fabricated by lithography approach.
- A 3D solid-state supercapacitor is demonstrated using polypyrrole coated interdigitated electrodes and polymer electrolyte.

Keywords: 3D supercapacitor, Solid-state, Interdigitated electrode, Printing, Selective Laser Melting Additive Fabrication.

1. Introduction

We are in the midst of rapidly growing information society with an insatiable demand for multifunctional portable/wearable electronic devices, including wireless sensors and even implantable medical devices [1]. Often, miniaturized power sources are essential to be integrated into such systems. Micro-batteries have been proved to be a promising solution for those applications [2-6]. Compared with batteries, supercapacitors have attracted significant attention due to their high power density and long cycle life [7]. Micro-supercapacitors, in particular are ideal for the high/pulsed power requirement in such devices [8-13].

Micro-supercapacitors based on the interdigitated structures [8-13] offer high charge storage capacity due to the ability for more material loading in the third dimension. Several MEMS technologies have been employed to fabricate 3D micro-supercapacitors [14-16]. Sun *et al.* designed a 3D interdigitated electrode using Lithography, Electroplating and Molding technology [14]. A single electrode with PPy coating showed a specific capacitance of 0.06 F cm^{-2} at a scan rate of 20 mV s^{-1}. The specific capacitance of the assembled 3D supercapacitor was 0.029 F cm^{-2} at a current density of 5 mA cm^{-2}. This group also produced 3D interdigitated electrodes utilizing a Deep Reactive Ion Etching method [15]. The electrode with PPy coating or the assembled symmetric supercapacitors exhibited a specific capacitance of 0.128 and 0.056 F cm^{-2} at a scan rate of 20 mV s^{-1}, respectively. Beidaghi *et al.*

built an interdigitated carbon micro-electrode array using the carbon-microelectromechanical (C-MEMS) approach [16]. The specific capacitance of the assembled micro-supercapacitor reached 75 mF cm^{-2} and the capacitance loss was less than 13% after 1000 cycles. These 3D carbon electrodes after PPy coating delivered a specific capacitance of 162.07±12.4 mF cm^{-2}. The assembled device showed the capacitance retention of 56% after 1000 cycles [17].

Overall, these fabrication processes have the disadvantages in requiring extensive and expensive machinery to produce 3D electrodes. In addition, harmful or toxic chemicals such as HF are used during the etching process [15]. Alternatively, Additive Fabrication approaches offer a simple and versatile route to fabricate even complex 3D electrode architectures. For example, a novel printing approach was reported to produce 3D micro Li-ion battery using an optimized ink with suitable composition and rheology [18].

In this work, we report the use of a 3D printing method called Selective Laser Melting (SLM) to produce 3D interdigitated Ti_6Al_4V electrodes. This Additive Fabrication process utilizes a high power laser to incrementally melt and fuse thin layers of metal powder to complete a 3D structure. It provides a facile and cost effective approach to produce both micro and macro structures, compared to the lithography method. PPy was electrodeposited on the vertical pillar surface as electroactive material. A symmetric solid-state pseudo-capacitor was demonstrated using poly(vinyl alcohol) (PVA)-H_3PO_4 polymer electrolyte.

2. Experimental

2.1 Materials

Pyrrole was sourced from Merck, sodium *p*-toluenesulfonate, PVA (Mw = 124,000-186,000 g mol^{-1}) were obtained from Sigma-Aldrich. Orthophosphoric acid (85%) was purchased from Ajax fine chemicals. Pyrrole was freshly distilled prior to use.

2.2 Fabrication of 3D interdigital electrodes and the solid-state supercapacitor

Designs were first drawn using Solidworks modelling software. The interdigitated electrodes were then built using a Realizer SLM50 metal printer (Realizer, Germany). The SLM printer is based on Selective Laser Melting in which free form metal parts are created by focusing a high-powered laser beam on a bed of fine metallic powder. The laser selectively fuses the particles in a layer by layer fashion. The Ti alloy was printed using a Ti-6AI-4V metal powder (TLS TechnikSpezialpulver). After printing the parts were removed from the build plate using an EDM wire cutting machine.

Ti electrodes for use were cleaned by sonication in Milli-Q water and ethanol. An Ag/AgCl reference electrode and a stainless steel mesh counter electrode were used during the PPy electropolymerization from an aqueous solution containing 0.1 M pyrrole and 0.1 M sodium *p*-toluenesulfonate at 0.75 V for 40 min. The electrodes were then rinsed with water and dried in a vacuum oven for 24 h at room temperature.

Copper wires were connected to the electrode bottom for electrical contact. The assembled supercapacitor was immersed into the PVA-H_3PO_4 solution for 2h under vacuum at room temperature to fill with electrolyte, and then dried in the fume hood for 12h. PVA-H_3PO_4 electrolyte was prepared as described in our previous report [19].

2.3 Characterization

The surface morphology of the electrodes was characterized by FE-SEM (JEOL JSM-7500FA). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) for single PPy electrode (top electrode) were carried out in a three-electrode system with a Pt mesh counter electrode and a Ag/AgCl reference electrode in 1.0 M Li_2SO_4 aqueous solution. CV was performed using CHI 650D (CHI Instruments) between -0.4 and 0.5 V. EIS was

measured using Gamry EIS 3000™ system in the frequency range of 100 kHz to 0.01 Hz with an AC perturbation of 10 mV at open circuit potential. Galvanostatic charge–discharge tests were performed using a battery testing system (Neware Electronic Co.) between 0 and 0.8 V.

3. Results and discussion

The design of the two halves of the interdigitated electrode is shown in Figure 1a. The electrodes have a rectangular footprint of 1 cm^2 with corresponding vertical posts spaced throughout. The bottom electrode consists of 33 posts and the top has 32. Each post has a 500 μm diameter and a 8 mm height. Four alignment posts with a 1.0 mm diameter and 10 mm height are built in the bottom electrode corner, while the top electrode provides 4 holes (～ 1.5 mm diameter). Partially welded metal particles are distributed on the individual post surface (Figure 1b), which may provide an enhanced surface area for polymerization. Each post was uniformly covered with a black layer of PPy film after the electropolymerization. PPy film displayed a cauliflower morphology composed of large nodules (Figure 1c).

The electrochemical properties of the PPy coated electrode (top electrode) was tested using cyclic voltammetry over the potential range of -0.4 to 0.5 V. The bare Ti_6Al_4V electrode showed negligible response (Figure 2a). PPy coated electrode displayed a nearly rectangular response at scan rates up to 50 mV s^{-1} (Figure 2b), which indicated that its charge-discharge processes were highly reversible and kinetically facile. At a scan rate of 100 mV s^{-1}, the rectangular CV shape became distorted. This may be attributed to the inclusion/ejection and diffusion of counter ions being slow compared to the electron transfer in the PPy matrix at high scan rates [20]. The volumetric capacitance decreased with an increase in scan rate as shown in Figure 2c. It can be explained by this system having insufficient time for ions to complete the doping-dedoping process at high scan rates. The electrode delivered a specific

capacitance of 10.1, 6.1, 4.6, 3.4 and 2.5 F cm^{-3} at a scan rate of 5, 10, 20, 50, 100 mV s^{-1}, respectively. The areal capacitance of PPy film was 0.057 F cm^{-2} at a scan rate of 20 mV s^{-1}, which was comparable to that delivered from the 3D micro structure created by Sun and co-workers [14].

The Nyquist plot of the electrode exhibited a compressed semicircle in the high frequency region and a line in the low frequency region (Figure 2d). This design was highly conductive as evidenced from the low bulk resistance (～1.8 Ω, the intercept point on the real axis) and low charge transfer resistance (～1.0 Ω, diameter of the semicircle).

The use of PVA-H_3PO_4 polymer electrolyte instead of liquid electrolyte can minimize electrolytes leakage [21], which is highly desirable for an integrated electronic system particularly in the case of a wearable system. The charge/discharge curves of our supercapacitor showed a nearly symmetrical triangular shape, indicative of good capacitor behavior. It presented a volumetric capacitance of 2.4 and 0.98 F cm^{-3} at a current density of 3.74 and 37.4 mA cm^{-3}, respectively (Figure 3b). The decrease in capacitance at high current density can be ascribed to the insufficient redox process. This device can provide a maximum energy density and power density of 213.5 Wh m^{-3} and 15.0 kW m^{-3} in a current density range of 3.74-37.4 mA cm^{-3}. The areal energy density of PPy film in our device was 2.98×10^{-6} Wh cm^{-2}, higher than 0.92×10^{-6} Wh cm^{-2} reported for the device composed of planar PPy electrodes and PVA-H_3PO_4 electrolyte [22]. This may be due to the enhanced surface area of our printed electrodes. Our device also demonstrated a good cycling stability with a 90% and 78% capacitance retention after 500, 1000 cycles, respectively at a current density of 14.98 mA cm^{-3}. This is higher than 56% retention after 1000 cycles reported for PPy coated 3D carbon electrodes supercapacitor [17].

Conclusion

A 3D interdigitated supercapacitor was fabricated using PPy coated Ti electrodes and PVA-H_3PO_4 polymer electrolyte. The 3D Ti electrodes were fabricated by a versatile printing method, Selective Laser Melting. PPy coated electrodes showed a comparable capacitance to the 3D electrodes fabricated by the lithography process. The assembled solid-state symmetric supercapacitor delivered a volumetric capacitance of 2.4 F cm^{-3}, an energy density of 213.5 Wh m^{-3} and a power density of 15.0 kW m^{-3} at a current density of 37.4 mA cm^{-3}. Currently, we can produce the micro-pillars with around 200 μm diameter at several mm in height with separation distance of around 300 μm. Future optimization could reduce the electrode array footprint, thereby improving printed miniaturized power sources. Novel electrode designs are readily created using CAD software and multiple electrodes can be realised in just a number of hours.

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References:

[1] J. Chmiola, C. Largeot, P.-L. Taberna, P. Simon, Y. Gogotsi, Science 328 (2010) 480.

[2] R.W. Hart, H.S. White, B. Dunn, D.R. Rolison, Electrochemistry Communications 5 (2003) 120.

[3] M. Nathan, D. Golodnitsky, V. Yufit, E. Strauss, T. Ripenbein, I. Shechtman, S. Menkin, E. Peled, Journal of Microelectromechanical Systems 14 (2005) 879.

[4] H.-S. Min, B.Y. Park, L. Taherabadi, C. Wang, Y. Yeh, R. Zaouk, M.J. Madou, B. Dunn, Journal of Power Sources 178 (2008) 795.

[5] H.C.M. Knoops, P.H.L. Notten, R.A.H. Niessen, L. Baggetto, W.M.M. Kessels, Journal of Materials Chemistry 20 (2010) 3703.

[6] N.A. Kyeremateng, F. Dumur, P. Knauth, B. Pecquenard, T. Djenizian, Electrochemistry Communications 13 (2011) 894.

[7] M. Winter, R.J. Brodd, Chemical Reviews 104 (2004) 4245.

[8] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna, P. Simon, Nature Nanotechnology 5 (2010) 651.

[9] C. Shen, X. Wang, W. Zhang, F. Kang, Journal of Power Sources 196 (2011) 10465.

[10] M. Xue, Z. Xie, L. Zhang, X. Ma, X. Wu, Y. Guo, W. Song, Z. Li, T. Cao, Nanoscale 3 (2011) 2703.

[11] M.F. El-Kady, R.B. Kaner, Nature Communications 4 (2013) 1475.

[12] P. Huang, M. Heon, D. Pech, M. Brunet, P.-L. Taberna, Y. Gogotsi, S. Lofland, J.D. Hettinger, P. Simon, Journal of Power Sources 225 (2013) 240.

[13] S. Makino, Y. Yamauchi, W. Sugimoto, Journal of Power Sources 227 (2013) 153.

[14] W. Sun, X. Chen, Microelectronic Engineering 86 (2009) 1307.

[15] W. Sun, R. Zheng, X. Chen, Journal of Power Sources 195 (2010) 7120.

[16] M. Beidaghi, W. Chen, C. Wang, Journal of Power Sources 196 (2011) 2403.

[17] M. Beidaghi, C. Wang, Electrochimica Acta 56 (2011) 9508.

[18] K. Sun, T.-S. Wei, B.Y. Ahn, J.Y. Seo, S.J. Dillon, J.A. Lewis, Advanced Materials 25 (2013) 4539.

[19] C. Zhao, C. Wang, Z. Yue, K. Shu, G.G. Wallace, ACS Applied Materials & Interfaces 5 (2013) 9008.

[20] B. Yue, C. Wang, X. Ding, G.G. Wallace, Electrochimica Acta 68 (2012) 18.

[21] W.H. Meyer, Advanced Materials 10 (1998) 439.

[22] S.A. Hashmi, R.J. Latham, R.G. Linford, W.S. Schlindwein, Polymer International 47 (1998) 28.

Figure Captions

Figure 1 (a) Schematic procedures used to fabricate solid state supercapacitors, including interdigitated Ti electrodes design, PPy electropolymerizayion and device assembly. SEM images of an individual Ti post surface (b) and after PPy coating (c) (Inset, at higher magnification).

Figure 2 (a) CV curves of PPy coated or uncoated Ti arrays electrode at a scan rate of 50 mV s^{-1}. (b) CV curves and (c) volumetric capacitances of PPy coated Ti arrays electrode at various scan rates. (d) Nyquist plot of PPy coated Ti arrays electrode.

Figure 3 Charge-discharge curves (a) and volumetric capacitances (b) at various current densities, Ragone plot (c) and capacitance retention (d) of the solid-state supercapactior.

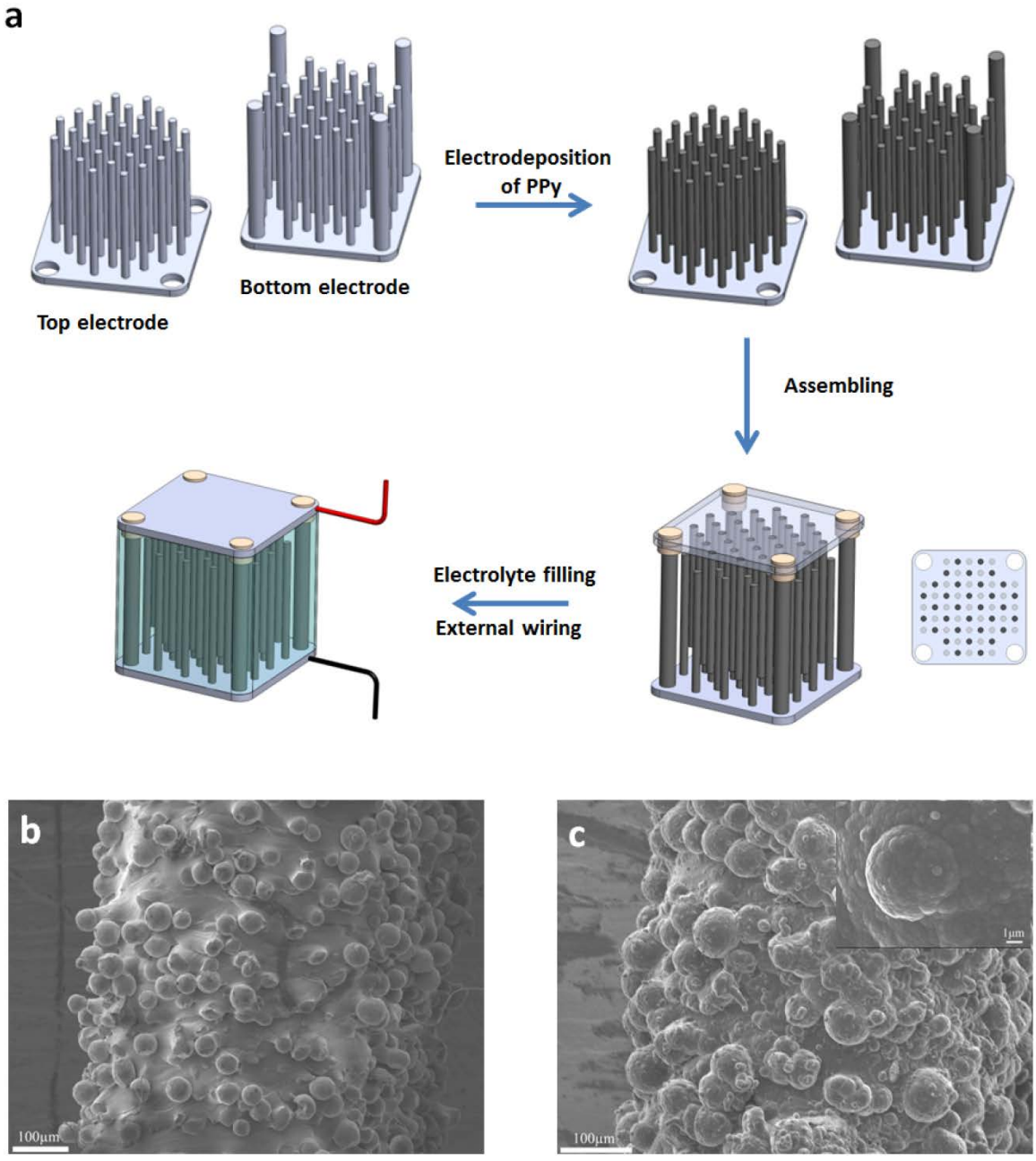
a
Top electrode
Bottom electrode
Electrodeposition
of PPy
Assembling
Electrolyte filling
External wiring
b
100μm
c
1μm
100μm

Figure 1

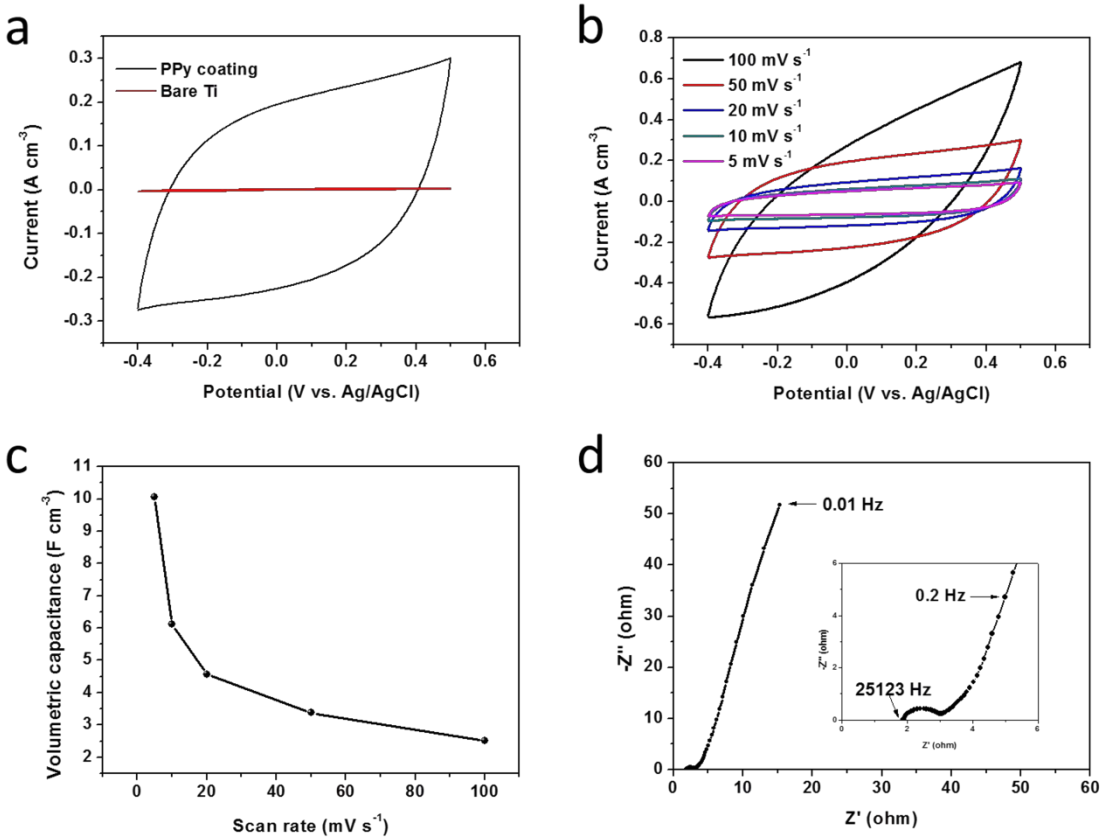
a
PPy coating
Bare Ti
Current (A cm-3)
Potential (V vs. Ag/AgCl)
b
100 mV s-1
50 mV s-1
20 mV s-1
10 mV s-1
5 mV s-1
Current (A cm-3)
Potential (V vs. Ag/AgCl)
c
Volumetric capacitance (F cm-3)
Scan rate (mV s-1)
d
0.01 Hz
0.2 Hz
25123 Hz
-Z'' (ohm)
Z' (ohm)

Figure 2

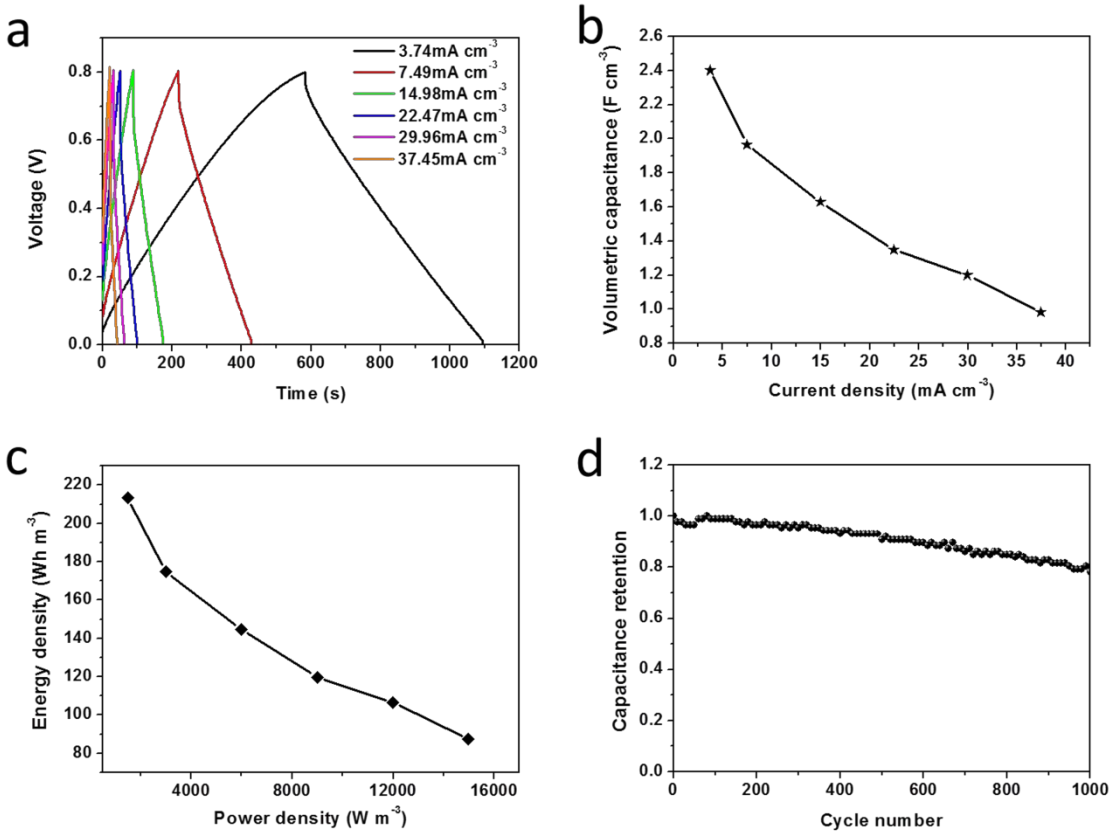
a
Voltage (V)
Time (s)
3.74mA cm-3
7.49mA cm-3
14.98mA cm-3
22.47mA cm-3
29.96mA cm-3
37.45mA cm-3
b
Volumetric capacitance (F cm-3)
Current density (mA cm-3)
c
Energy density (Wh m-3)
Power density (W m-3)
d
Capacitance retention
Cycle number

Figure 3